

Identification of polymorphs of pentacene

Christine C. Mattheus ^a, Anne B. Dros ^a, Jakob Baas ^a, Gert T. Oostergetel ^a, Auke Meetsma ^a, Jan L. de Boer ^a, and Thomas T. M. Palstra ^{a*}

^aSolid State Chemistry Laboratory, Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG Groningen, the Netherlands.

Pentacene crystallizes in a layered structure with a herringbone arrangement within the layers. The electronic properties depend strongly on the stacking of the molecules within the layers [1]. We have synthesized four different polymorphs of pentacene, identified by their layer periodicity, $d(001)$: 14.1, 14.4, 15.0 and 15.4 Å. Single crystals commonly adopt the 14.1 Å structure, whereas all four polymorphs can be synthesized in thin film form, depending on growth conditions. We have identified part of the unit cell parameters of these polymorphs by X-ray and electron diffraction. The 15.0 and 15.4 Å polymorphs transform at elevated temperature to the 14.1 and 14.4 Å polymorphs, respectively. Using SCLC measurements, we determined the mobility of the 14.1 Å polymorph to be 0.2 cm²/Vs at room temperature.

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Introduction

Pentacene has recently gained interest as a molecular conductor with a very high electronic mobility. Mobilities of 1 cm²/Vs were reported at 300K, increasing to 10⁴ cm²/Vs at low temperatures [2]. Moreover, evidence for superconductivity up to 2 K in field effect devices was reported [3]. We study the origin of this high mobility and its relation with the crystal structure, *i.e.* the stacking of the molecules. The crystal structure and growth of pentacene has been subject of a number of studies [4,5,6,7,8]. Pentacene crystallizes in a layered structure with a herringbone arrangement within the layers, see Fig. 1. The layer periodicity, $d(001)$, is by far the largest repeat unit, and thus characteristic of the structure. In the early sixties, Campbell *et al.* determined the single crystal structure using a film method [9]. These results were slightly modified [10], but yielded both a characteristic $d(001)$ value of 14.4 Å. In 1991 Minakata *et al.* reported on the growth and crystal structure of thin films [11,12]. They reported for thin films

$d(001)$ -spacings of 15.0 and 15.4 Å. It was only noticed by Dimitrakopoulos *et al.* [13] that these thin film polymorphs must be different from the single crystal. They also observed for the first time the coexistence of two phases, of 14.4 and 15.4 Å. The growth of these polymorphs was studied by Schoonveld *et al.* [4,5]. These phases are generally referred to as the "single crystal" and "thin film" phase. We argue the former name to be incorrect as more recent redeterminations of the single crystal structure by Holmes *et al.* [8], Siegrist *et al.* [14] and by us [15] show the single crystal $d(001)$ value to be 14.1 Å. Apparently there exist several polymorphs of pentacene. Identification of these pentacene polymorphs is especially important when the electronic properties are related to the crystal structure. Recent band structure calculations show that the electronic properties depend strongly on the particular stacking of the molecules within the layers [1]. In this paper we discuss how the various polymorphs can be made, and what their crystal structures are. We identify four different polymorphs and determine by X-ray and electron diffraction their unit cell parameters. Of one of the polymorphs we determine the hole mo-

*Corresponding author. Tel.: +31-50-363-4440; fax: +31-50-363-4441. E-mail: T.T.M.Palstra@chem.rug.nl

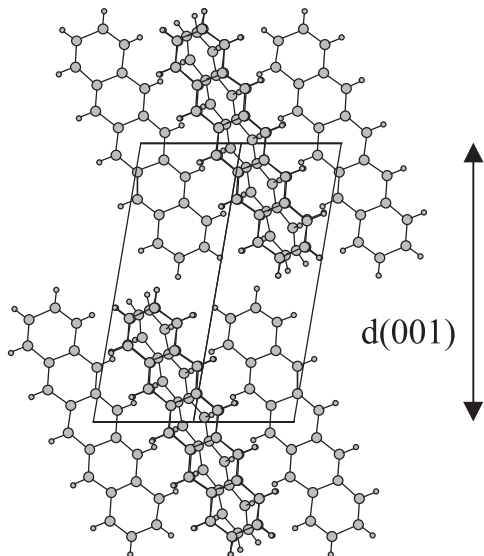


Figure 1. *The crystal structure of single crystalline pentacene. The view along the $[1\bar{1}0]$ axis shows the layered structure, the unit cell is also indicated.*

bility, *via* space-charge-limited-current measurements on a single crystal.

Experimental procedures

Thin films of pentacene were prepared by evaporation in a high vacuum environment of 10^{-7} mbar. The source material, pure pentacene was obtained from Aldrich and not further purified. It was placed in a tantalum crucible and heated to 540 K. As substrate thermally oxidized silicon (α -SiO₂) or kapton (polyimide) was used. The substrate temperature was measured with an Al-Cr thermocouple and the substrate could be heated or cooled. The evaporation rate of the sublimed material was monitored by a quartz oscillator and the layer thickness was determined using a dektak. The evaporation was kept constant at a low rate of 0.1 nm/sec to ensure crystallinity. A shutter allowed the evaporation rate to become stable before the substrate was ex-

posed to the pentacene flow.

Single crystals of pentacene were grown using a vapour transport method [16]. A pyrex tube was thoroughly cleaned by heating it under a stream of pure nitrogen gas. 200 - 400 mg of unprocessed pentacene, obtained from Aldrich, was placed at one end of the tube in a platinum crucible. The growth was performed either under a stream of nitrogen gas mixed with hydrogen gas, with a volume percentage of 5.1(1)% hydrogen, or under an argon flow. Transport gases were obtained from AGA with 5N purity for N₂ and Ar and 4N5 purity for H₂. Great care was taken to avoid contamination with O₂ and H₂O. Nitrogen and argon gases were further purified over activated copper and alumina columns. A temperature gradient was applied by resistively heating two heater coils wrapped around the tube. Crystallization took place some 300 mm from the sublimation point at a temperature of approximately 490 K. Single crystals were also grown from a solution of trichlorobenzene (TCB). Violet crystals were obtained by slowly (four weeks) evaporating the TCB at 450 K, under a stream of ultra pure nitrogen gas.

The X-ray diffraction patterns of the obtained single crystals were measured with an Enraf-Nonius CAD-4 or a Bruker SMART APEX diffractometer. Both diffractometers use monochromated Mo - K α radiation. The structures are solved using SHELXS and SHELXL [17]. The X-ray diffraction patterns of pentacene thin films were measured using a D8 powder diffractometer of Bruker A.G. in a Bragg-Brentano geometry, with monochromatic Cu-K α radiation. A variable temperature stage is used for in situ temperature dependent measurements between 100 K and 650 K, in a vacuum of 10^{-2} mbar. The obtained spectra were analyzed using the TOPAS software package [18]. Electron diffraction (ED) measurements were performed on a Philips CM200/FEG (200 kV) transmission electron microscope. During the measurements the electron dose was held low, to prevent radiation damage of the samples. Experiments were performed in the Electron Microscopy group of the department of biophysical chemistry in Groningen and in the National Centre for HREM

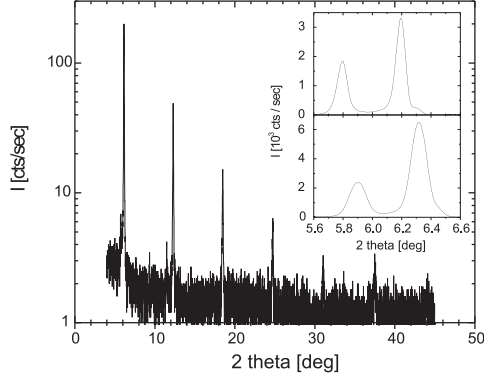


Figure 2. X-ray diffraction pattern for a pentacene thin film grown at 353 K on thermally oxidized a -SiO₂. The reflections can be indexed as $(00l)$, with a $d(001)$ spacing of 14.42 Å. Inset, top: part of a X-ray spectrum of a thin film grown on a -SiO₂. The observed reflections correspond to $d(001)$ values of 15.4 and 14.4 Å. This specific (2.5 μm thick) sample also contains a small amount of the 14.1 Å phase, as calculated from the shoulder of the reflection at 6.19°. Inset, bottom: part of a X-ray spectrum of a thin film grown on kapton. The reflections correspond to $d(001)$ values of 15.0 and 14.1 Å. The broader peak shape for the films grown on kapton indicates a larger mosaic spread of these films.

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Growth of the different polymorphs on thin films

In the literature different $d(00l)$ values are reported for pentacene thin films [4,11,12,19]. To investigate this, we have grown thin films of pentacene, using different growth conditions. A typical X-ray diffraction pattern of a pentacene thin film is shown in Fig. 2. The peaks can be indexed as $00l$ reflections, indicating a strong preferential alignment with the $[00l]$ vector perpendicular to the substrate.

In the inset of Fig. 2, parts of two diffraction patterns of two thin films, grown in different

ways, are shown. We observe reflections centered at 5.80, 5.92, 6.19 and 6.33 degrees 2θ . Analysis of the entire spectra shows the reflections to correspond to $d(001)$ spacings of 14.1, 14.4, 15.0 and 15.4 Å. This result indicates that at least four polymorphs of pentacene are present in the various thin films.

Typically, two polymorphs are observed on one thin film sample, as shown in the inset of Fig. 2. However, single phased thin films can be grown. In literature the growth of the 14.4 and 15.4 Å polymorphs was reported to depend on the film thickness and the substrate temperature [4,5]. We observe that the growth of the polymorphs depends also on the nature of the substrate. The 14.4 and 15.4 Å polymorphs grow on a -SiO₂ substrates, whereas the 14.1 and 15.0 Å polymorphs grow on kapton. The top of the inset in Fig. 2 shows a part of a spectrum of a film grown on a -SiO₂. In this spectrum we observe the 14.4 and 15.4 Å polymorphs. At the bottom of this figure, the pattern of a film grown on kapton is shown. Here, peaks correspond to the 14.1 and 15.0 Å polymorphs.

The 15.4 Å phase can be grown single phased if the film thickness remains below a certain critical value, which depends on the substrate temperature. This polymorph is typically grown at room temperature. The 14.4 Å phase is observed above this critical thickness, and at an elevated substrate temperature. The fraction of this polymorph increases with the film thickness [4,5]. We observe that this dependence on the substrate temperature and the film thickness also holds for the 15.0 and 14.1 Å polymorphs. Here, the 15.0 Å polymorph is stable for small film thicknesses and low substrate temperatures.

Typical growth conditions to obtain single-phased films are listed in Table 1. We have grown single phased films of the 15.0 and 15.4 Å phases at ambient temperature with a film thickness of approximately 50 nm, on a kapton and a -SiO₂ substrate, respectively. The 14.1 and 14.4 Å phases were observed single-phased on films grown at 370 K, with a thickness of ~150 nm, on substrates of kapton and a -SiO₂, respectively.

The spectrum on the top of the inset in Fig. 2

	50 nm at 300 K	150 nm at 350 K
<i>a</i> -SiO ₂	15.4	14.4
kapton	15.0	14.1

Table 1

Typical conditions for single-phase growth of the specific pentacene polymorphs.

was of a 2 μm thick film. In this spectrum we observe not only two, but three polymorphs of pentacene. Besides the 15.4 and 14.4 \AA polymorphs, the shoulder of the peak at $6.19^\circ 2\theta$ could be recognized as belonging to the 14.1 \AA structure. This suggests that the growth of the different phases on an *a*-SiO₂ substrate is as follows. In the first ~ 30 monolayers the 15.4 \AA polymorph is formed, if the film becomes thicker also the 14.4 \AA structure appears. If the film becomes extremely thick (>1300 monolayers), also the 14.1 \AA phase is observed. The 14.1 \AA structure is observed in single crystals and on thin films grown on polyimide. This substrate does, therefore, not seem to influence the growth. However, the appearance of the 14.1 \AA polymorph on thick films on a *a*-SiO₂ substrate indicates that the 14.4 and 15.4 \AA polymorphs are substrate induced.

Temperature dependence

We studied the possibility of structural phase transitions between 143 and 423 K. Firstly, a film of the 15.4 \AA structure was measured at ambient temperature, slowly heated to 403 K and cooled down again. An irreversible change of the 15.4 \AA phase into the 14.4 \AA phase was observed. This structural change as function of temperature is shown in Fig. 3. In this figure relative intensities are shown, because above 370 K sublimation of the material started. This decreases the measured intensity and makes the structural change difficult to observe.

Heating a film containing both the 15.0 and the 14.1 \AA phases, to 423 K, showed behaviour analogous to the 15.4 \AA phase. At elevated temperatures the 15.0 \AA phase changed irreversibly into the 14.1 \AA structure.

We cooled and heated the 14.1 \AA polymorph

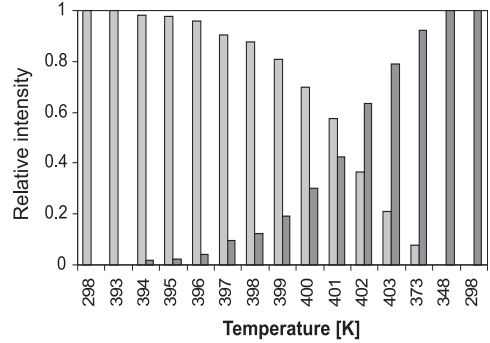


Figure 3. *The relative intensity of the 15.4 and 14.4 \AA phases for a temperature sequence. Light grey: 15.4 \AA , dark grey: 14.4 \AA .*

in single and poly-crystalline form. A full single crystal data set was measured at 90 K. However, no phase transition was observed. From the temperature dependence of X-ray spectra of powder of the 14.1 \AA polymorph, in the range of 143 K to 475 K, we derive anisotropic linear coefficients of thermal expansion: $\alpha_a = -19 \cdot 10^{-6} \text{ K}^{-1}$, $\alpha_b = 64 \cdot 10^{-6} \text{ K}^{-1}$, and $\alpha_c = 53 \cdot 10^{-6} \text{ K}^{-1}$.

A film containing only the 14.4 \AA polymorph was slowly heated to 475 K, but no structural transition was observed. We cooled a sample containing both the 15.4 and the 14.4 \AA polymorphs to 143 K. No structural changes were observed during the cooling process. Also a film containing the 15.0 \AA and 14.1 \AA polymorphs did not show any structural transition during cooling. From these experiments it can be concluded that the 14.1 and the 14.4 \AA phases are thermally the most stable ones. The 15.0 and 15.4 \AA structures can, at elevated temperatures, be transformed into the 14.1 and 14.4 \AA phases, respectively.

It was already observed by Gundlach *et al.* that the 15.4 \AA phase can be transformed into the 14.4 \AA polymorph [6]. They exposed their films of the 15.4 \AA phase to solvents like acetone, isopropanol, and ethanol (in which pentacene does not dissolve) and noticed that the 15.4 \AA phase almost completely changed to the 14.4 \AA phase. We performed the same experiments and observed

that indeed the 15.4 Å phase disappeared from the spectra. Since we lost some material in the process, it was not clear whether it was transformed into the 14.4 Å phase or had become amorphous. The same observation was made for the 15.0 Å polymorph, which transformed after exposing the film for ~ 3 minutes to ethanol.

The 14.1 Å polymorph: single crystals

Besides the growth of thin films, also single crystals were grown. Single crystals, grown in various ways, yield exclusively the 14.1 Å polymorph. Crystal growth from vapour transport yields almost centimeter sized violet crystals, in different forms: platelets and needles. These pentacene single crystals were measured on the CAD-4 diffractometer. Needle shaped crystals were observed to grow along the $[1\bar{1}0]$ axis, whereas the platelets grow in the ab plane. Both had a $d(001)$ value of 14.1 Å. Pentacene single crystals grown from a solution of trichlorobenzene were analyzed on the APEX diffractometer. This yielded the same crystal structure as for the crystals grown using the vapour transport technique. The unit cell parameters are given in Table 2 and more details are reported elsewhere [15,20].

The vapour transport experiments did not result in single crystals of pentacene exclusively. The employed transport gases, and their flow rate, were of significant influence on the crystals. At a slightly lower temperature (480 K) than where the violet pentacene crystals crystallized, also red needles were grown. If excess hydrogen gas was used, more red crystals were observed. The crystallization point was ~ 50 mm apart from the centre of the pentacene growth, which allowed physical separation of the two types of crystals. Single crystal diffraction showed it to be a hydrogenated form of pentacene: 6,13-dihydropentacene, with two methylene groups at opposite sides of the middle ring. The structure can be described as a monoclinic unit cell containing four non-planar hydrogenated pentacene molecules and two planar pentacene molecules. The detailed crystal structure is described elsewhere [20].

At lower hydrogen content, or if no ultra

pure inert transport gas was used, yellow-brown coloured crystals could be observed. They condense at a slightly higher temperature than the pure pentacene crystals, at ~ 520 K. Analysis on the APEX diffractometer proved it to be an oxidized form of pentacene, 6,13-pentacenequinone, with two carbonyl groups at opposite sides of the middle ring. The unit cell is monoclinic, and described elsewhere [20], in agreement with literature [21].

The 14.4 Å polymorph: powder diffraction

The 14.4 Å polymorph was grown by vacuum sublimation on α -SiO₂ at 363 K. The Bragg-Brentano diffraction pattern indicated that the 2 μ m thick film contained mostly the 14.4 Å structure, with small amounts of 15.4 and 14.1 Å polymorphs. The 15.4 Å phase was removed using Gundlachs method [6] of dipping the film in ethanol. A new diffraction pattern confirmed this. The film was mechanically removed from the substrate and ground into a powder. The powder was dispersed on Scotch tape and remeasured in a transmission geometry on the Bruker D8 diffractometer. The powder diffraction pattern at room temperature is shown in Fig. 4.

Clearly, reflections other than $00l$ can be observed. The unit cell parameters were analyzed, while the fractional coordinates were not further refined. The pattern can be fitted with a mixture of two phases. The majority phase (91%) was found to have unit cell parameters which are listed in Table 2, and yields a $d(001)$ of 14.37 Å. A minority phase could be indexed with the 14.1 Å single crystal unit cell.

The 15.0 and 15.4 Å polymorphs: electron diffraction

Because the 15.0 and 15.4 Å polymorphs can only be grown for small film thickness, insufficient sample was available for X-ray powder diffraction. Here, we used electron diffraction (ED) to obtain structural information.

We performed electron diffraction experiments in a transmission geometry. ED has the advantage above X-ray based techniques, that the in-

	a	b	c	α	β	γ	$d(001)$
Single Crystal 300K	6.266(1)	7.775(1)	14.530(1)	76.475(4)	87.682(4)	84.684(4)	14.12
Single Crystal 90K	6.239(1)	7.636(1)	14.330(2)	76.978(3)	88.136(3)	84.415(3)	13.96
Powder diff.	6.485(1)	7.407(2)	14.745(4)	77.25(2)	85.72(2)	80.92(2)	14.37

Table 2: The lattice parameters of the 14.1 and 14.4 Å pentacene polymorphs. The data of the single crystal polymorph are listed for both 90 K and 300 K.

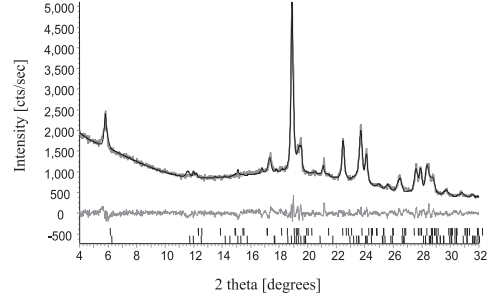


Figure 4. Observed (grey) and simulated (black) diffraction pattern of a 2.5 μm thick film of pentacene, grown on $\alpha\text{-SiO}_2$ at 363 K, and removed from its substrate. The pattern consists of a majority (91%) 14.4 Å polymorph and a minority (9%) 14.1 Å polymorph. The difference spectrum is shown by the gray line under the spectrum. All reflections could be indexed, but the parameter set was too large to fit the intensities and obtain fractional coordinates for the 14.4 Å structure.

cident beam can be focussed. The scattering cross section is large, and can thus probe very small areas. In our ED experiments an electron beam with a diameter of 0.3 μm is used. Atomic force microscopy pictures of thin films show that films made at room temperature typically have a crystal size of 0.2 - 0.3 μm . Films grown at a higher temperature are more crystalline, and exhibit crystal sizes up to 1 μm . Electron diffraction offers thus the possibility to perform diffraction experiments on one single crystal area instead of a polycrystalline sample.

Samples for ED were prepared by evaporating a pentacene layer on a copper grid, which is covered with a carbon film. The pentacene layer of ~ 100 nm, was evaporated on a substrate which was held at 345 K. When a single crystal area is located on the sample, the ED image exhibits spots instead of circles, as shown in Fig. 5. X-ray diffraction experiments showed strong preferential orientation with the $[00l]$ axis. Therefore it is likely that the spot patterns observed with ED, in

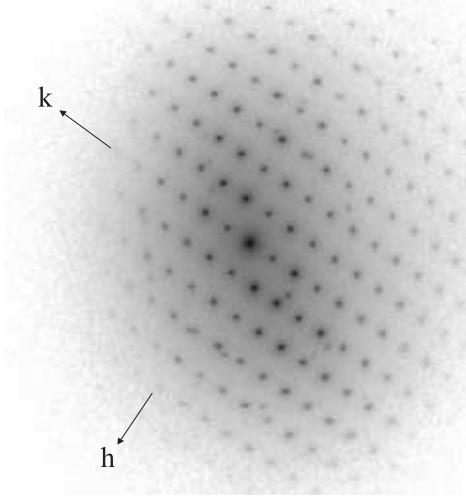


Figure 5. Transmission electron microscopy pattern. A typical projection of a $(hk0)$ plane is shown.

transmission, are generated by the $(hk0)$ planes. From this diffraction pattern, the reciprocal lattice parameters a^* , b^* and γ^* can be determined. This measurement was calibrated by measuring a gold sample as reference. Various diffraction measurements, on different locations on the same sample, resulted in three different sets of \mathbf{a}^* , \mathbf{b}^* and γ^* values. We observed on an edge of the same sample also one \mathbf{c}^* value. The results are listed in Table 3. The reciprocal lattice data of the single crystal and the ED results calculated from Minakata *et al.* [7] have been added to this table. Note that the difference between \mathbf{a}^* and $-\mathbf{a}^*$ or \mathbf{b}^* and $-\mathbf{b}^*$ could not be observed. Therefore a γ^* value of 89° can also be 91° .

We observe all four polymorphs of pentacene on the same sample. In the first set of observed values (ED1, see Table 3) the \mathbf{a}^* and \mathbf{b}^* values correspond to the single crystal data. The γ^* value, however, deviates beyond the measuring precision from the value determined with single crystal diffraction. We have no explanation for

	a^*	b^*	c^*	α^*	β^*	γ^*	$d(001)$
SXD	0.1603	0.1328	0.0708	103.374	91.1114	94.91	14.12
ED1	0.1610	0.1319				89.5	
XRD	0.1563	0.1399	0.0696	102.25	92.37	98.4	14.37
ED2			0.0694				14.4
ED3	0.173	0.134				89	
Minakata ⁽¹⁾						90	
ED4	0.174	0.135				89.5	
XRD	0.180	0.140					15.0
XRD							15.4

Table 3: The reciprocal lattice parameters of pentacene, values are in \AA^{-1} . $d(001)$ values are in \AA . Each line lists an experiment, performed on different samples or different parts of a sample. SXD is single crystal X-ray diffraction, XRD is powder X-ray diffraction, ED means electron diffraction. (1): data calculated from Minakata *et al.* [7].

this difference and neglect it. The 14.4 Å phase was present, as an observed c^* value (ED2) indicates the presence of this polymorph. The third set of parameters observed in our ED experiments (ED3) is in good agreement with the values observed by Minakata *et al.* However, their reported c^* value was measured on a sample grown under the same conditions, but on a different substrate. Since we observed the nature of the substrate to be of crucial importance to the growth of a specific polymorph, we omit their reported value of c^* . ED4 in Table 3 lists a third set of a^* , b^* and γ^* values. These sets of data, ED3 and ED4, will belong to the 15.0 and 15.4 Å polymorphs.

In these experiments the electron beam was perpendicular to the substrate. By tilting the sample other reciprocal lattice vectors can be brought in diffraction condition. If sufficient hkl spots are identified, the unit cell can be constructed. However, the tilting may not change the small single crystalline area under study. Presently, tilting did affect the sample position, and we could not ascertain that the diffraction pattern belonged to the same polymorph. Furthermore, after a short exposure to the electron beam, the material suffered from radiation damage. Future modifications of the apparatus will allow to tilt the sample while keeping the same crystal in the beam.

Charge transport properties of the 14.1 Å polymorph.

We have used space-charge-limited-current measurements on single crystals of pentacene to determine the hole mobility of the 14.1 Å polymorph. Single crystals were grown under an argon atmosphere as described earlier. Rectangular shaped crystals (platelets) were glued onto glass substrates using GE-varnish. Contacts were applied using a shadow mask. Stripes of 10 nm titanium and 40 nm gold were evaporated in a high vacuum environment. Distances between the stripes were 50 or 75 μm . Measurements were performed in the ab plane. Platinum wires were connected to the stripes with silver epoxy. The epoxy was cured at 70°C in air for 10 minutes. The crystals were exposed to air for ap-

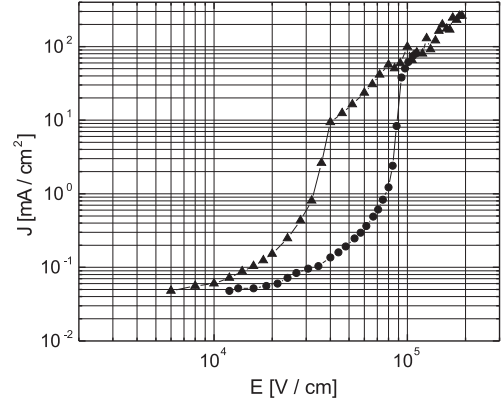


Figure 6. *Current-voltage characteristic of single crystalline pentacene (14.1 Å polymorph). Δ : gap of 50 μm , \bullet : gap 75 μm .*

proximately one hour before they were placed in vacuum. Samples were measured in darkness and a vacuum of $2 \cdot 10^{-7}$ mbar. As measuring device a Keithley 2410 high voltage sourcemeter was used. The $J(E)$ characteristics were measured using a pulsed staircase sweep with a pulsewidth of 0.3 sec.

The $J(E)$ measurements can be seen in Fig. 6. The results of these current-voltage measurements can be described using the standard semiconductor band model [22]. We assume holes to be the majority carriers in the crystals. From analysis of the curves [22,2] we calculated the hole mobility, trap density, the energy of the trap level and the acceptor density: $\mu = 0.2 \text{ cm}^2/\text{Vs}$, $N_t = 2 \cdot 10^{13} \text{ cm}^{-3}$, $E_t = 580 \text{ meV}$ and $N_a = 4 \cdot 10^{12} \text{ cm}^{-3}$.

Conclusion

Pentacene has been shown to crystallize in four different polymorphs. These different structures can be identified by their $d(001)$ value, which is characteristic for the structure. Values of 14.1, 14.4, 15.0 and 15.4 Å have been observed. Single crystals commonly adopt the shortest $d(001)$ spacing of 14.1 Å. All four polymorphs can be made as thin films. The growth of the different polymorphs as thin films was shown

to depend strongly on the substrate, substrate temperature and film thickness. The 14.4 and 15.4 Å polymorphs appear to be induced by the substrate.

Temperature dependent X-ray diffraction measurements showed that the 14.1 and 14.4 Å phases are the most stable. The 15.0 and 15.4 Å structures are less stable and can be changed into 14.1 and 14.4 Å, respectively, at elevated temperatures or by exposing them to solvents. There is no indication of a structural phase transition in the 14.1 and 14.4 Å phases in the temperature range of 143 - 473 K.

Pentacene single crystals have been grown, both by vapour transport methods and from solution. The crystal structure that we report [15] agrees with the analysis of Holmes *et al.* [8] and Siegrist *et al.* [14], but is distinctly different from the data reported by Campbell *et al.* [9,10].

Pentacene is during crystal growth sensitive to both oxidation and hydrogenation, resulting in single crystals of dihydropentacene and pentacenequinone. The methylene and carbonyl groups are located at opposite sides of the middle ring, which seems the most reactive.

Powder diffraction experiments were used to obtain the unit cell parameters of the 14.4 Å polymorph. Electron diffraction experiments revealed for three polymorphs the \mathbf{a}^* , \mathbf{b}^* and γ^* values.

Using SCLC measurements we determined the mobility of the 14.1 Å polymorph of pentacene to be 0.2 cm²/Vs. Furthermore, these measurements show our single crystals to be very pure, having only 10¹³ traps cm⁻³.

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